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Anthracene mediated electrochemical synthesis of metallic cobalt nanoparticles in solution

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ABSTRACT

The metallic cobalt nanoparticles in the bulk solution were obtained by antracene mediated reduction of $[CoCl_4]^{2-}$ in the potentiostatic electrolysis in an undivided cell at the potential of the anthracene reduction to radical anion at room temperature in DMF/0.1 M Bu_4NCl media. $[CoCl_4]^{2-}$ ions are generated by the sacrificial cobalt anode dissolution during the electrolysis. The metal particles are oxidized upon contact with the air to form the oxidized cobalt nanoparticles with a low dispersity (20–30 nm).

1. Introduction

In recent years, the metal nanoparticles are of great scientific interest due to their unique physical and chemical properties different from those of bulk metals, and a wide variety of potential applications in the field of catalysis, biomedicine, optics, electronics and other [1–7]. Methods of preparation of metal nanoparticles are quite diverse. They are conventionally divided into physical, chemical and sometimes into biochemical ones. The electrochemical methods of obtaining of metal nanoparticles in solution have found only limited application [6–14], although the electrochemical reduction of the metal ions and complexes is the classical method of producing metals, metal plating, metal black on the electrode surface on an industrial scale [15]. This is primarily because the direct reduction of metal ions results in metal deposition on the electrode surface. For example, when using this method of producing silver nanoparticles in solution, up to 80 percent of the metal is deposited on the electrode surface [11]. The problem of deposition is partially solved by a combination of the metals accumulation process during a short current impulse followed by the metal transfer from the surface into the solution by means of sonification of the working electrode (pulse sonoelectrochemistry) [12–14].

It seems that another more efficient approach to implementation of the electrochemical process for production of metal and metal-alloy nanoparticles in solution can be a transfer of electroreduction reaction of ions or their complexes from the electrode surface into the solution using mediators. In the process of chemical synthesis of a finely-dispersed metal using alkali metals to reduce metal salts in ethereal or hydrocarbon solvents according to Rieke process, organic electron carriers (naphthalene, biphenyl, anthracene, etc.) are widely used as mediators [16–19]. The idea of using organic electron carriers for generating highly reactive metal (0) in solution by mediated electrochemical reduction of metal ions and metal complexes have been used by us to create highly efficient electrocatalytic systems for reduction of various organic substrates [20]. Based on this idea [20] recently an efficient electrosynthesis of palladium and silver nanoparticles have been carried out by the mediated reduction of $[PdCl_4]^{2-}$ in 60% aqueous DMF [21,22] and DMSO [23], anode-generated silver ions Ag^+ in DMF [24] using methylviologen MV^{2+} and/or tetraviologen calix[4]resorcine MVCA-C_n^{8+} (n = 1,5,10) with n-alkyl substituents in the resorcinol cycles as a mediator at potential of redox couples $MV^{2+}/MV^{\bullet+}$, MVCA-C_n^{8+}/MVCA-$C_n^{4\bullet+}$. Tetraviologen calix[4]resorcines also stabilized nanoparticles both in the solution and/or on the electrode surface. In this article, the electrochemical synthesis of cobalt nanoparticles in DMF/0.1 M Bu_4NCl using anthracene as a mediator is reported. Nanoparticles of cobalt and its alloys are of interest as catalysts [16,18] and magnetic materials [19,25]. Co^{2+} ions are reduced harder than the above-mentioned ions, so a reducing agent more effective than methylviologen radical cation is required to reduce them. Therefore, the choice of a medium and a mediator is made on the basis of earlier [20] findings of the reduction of cobalt ions by anthracene radical anion.

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